

# Development of an efficient alternative to recovery O<sub>2</sub> from metabolic CO<sub>2</sub> via electrolysis operated at ambient temperature and driven by a highly selective catalysis

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The current State of Art (SOA) on oxygen recovery onboard the Environmental Control and Life Support System (ECLSS) at the International Space Station (ISS) is complex, heavy, and power consuming system that recovers approximately 50% of the oxygen (O<sub>2</sub>) from metabolic carbon dioxide (CO<sub>2</sub>). For future long duration beyond low earth orbit missions (LEO), O<sub>2</sub> recovery systems will need to be highly reliable, efficient, and recover a minimum of 75% O<sub>2</sub> from metabolic CO<sub>2</sub>. An alternative technology development effort currently underway at NASA Marshall Space Flight Center (MSFC) has the potential to significantly increase O<sub>2</sub> recovery currently limited to 50% (Sabatier) and reduce the complexity of ECLSS O<sub>2</sub> recovery. MSFC and University of Texas in Arlington (UTA) have jointly designed and fabricated a microfluid electrochemical reactor (MFECR) that operates at ambient conditions and utilizes a proprietary catalysis highly selective on reducing CO<sub>2</sub> to ethylene (C<sub>2</sub>H<sub>4</sub>) at the cathode while O<sub>2</sub> is generated at the anode. The MFECR would replace three pieces of hardware for future ECLSS architectures: the current CO<sub>2</sub> Reduction Assembly (CRA) (Sabatier reactor), the Plasma Pyrolysis Assembly (PPA), and the Oxygen Generation Assembly (OGA). It is designed to interface directly with the CO<sub>2</sub> Removal Assembly (CDRA) and the Water Processing Assembly (WPA) to supply CO<sub>2</sub> reactant and water replenish respectively. This is expected to substantially improve sustainability of the ISS ECLSS and reduce requirement on power and weight. Here, we discuss the current development and evaluation efforts on different alternatives on not only the configuration and setup of the MFECR at an Engineering Design Unit (EDU) scale but also the selection of component materials.

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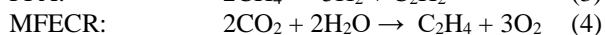
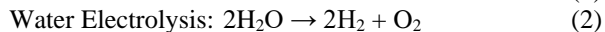
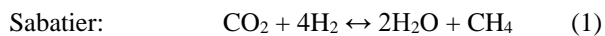
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## Nomenclature

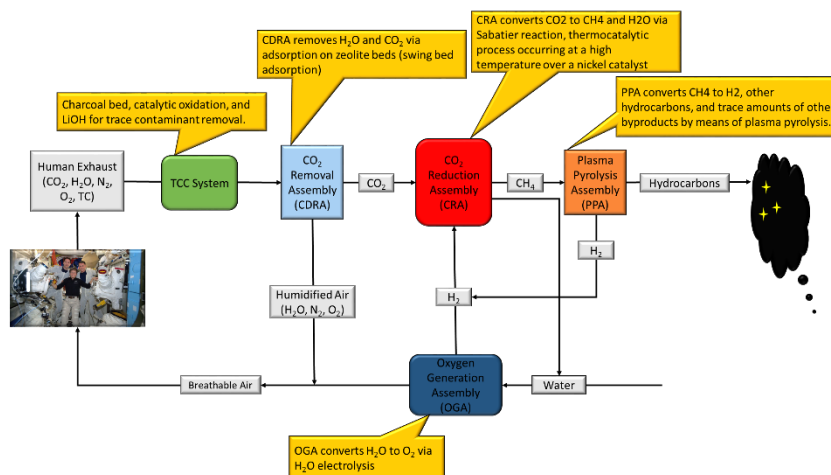
<i>AR</i>	=	atmospheric revitalization
<i>BPR</i>	=	back pressure regulator
<i>CDRA</i>	=	carbon dioxide removal assembly
<i>CRA</i>	=	carbon dioxide reduction assembly
<i>CO<sub>2</sub>R</i>	=	carbon dioxide reduction
<i>CO<sub>2</sub></i>	=	carbon dioxide
<i>C<sub>2</sub>H<sub>4</sub></i>	=	ethylene
<i>C<sub>2</sub>H<sub>2</sub></i>	=	acetylene
<i>CH<sub>4</sub></i>	=	methane
<i>CL</i>	=	catalysis layer
<i>EC</i>	=	electrochemical
<i>EDQ</i>	=	electrodeposition charge
<i>ECRo</i>	=	Electrolytic O <sub>2</sub> Recovery
<i>EDU</i>	=	engineering design unit
<i>ECLSS</i>	=	environmental control and life support system
<i>GC</i>	=	gas chromatograph
<i>GDL</i>	=	gas diffusion layer
<i>GDE</i>	=	gas diffusion electrode
<i>CL</i>	=	catalysis layer
<i>HER</i>	=	hydrogen evolution reaction
<i>KOH</i>	=	potassium hydroxide
<i>MEA</i>	=	membrane electrode assembly
<i>MFECR</i>	=	macrofluidic electrochemical reactor
<i>MPL</i>	=	macropore layer
<i>MSFC</i>	=	Marshall Space Flight Center
<i>NASA</i>	=	National Aeronautics and Space Administration
<i>N<sub>2</sub></i>	=	nitrogen
<i>OGA</i>	=	oxygen generation assembly
<i>OER</i>	=	oxygen evolution reaction
<i>O<sub>2</sub></i>	=	oxygen
<i>OH<sup>-</sup></i>	=	hydroxide ion
<i>PDE</i>	=	partial differential equations
<i>Pt</i>	=	platinum
<i>PTFE</i>	=	poly-tetra-fluoro-ethylene
<i>H<sub>2</sub></i>	=	hydrogen
<i>ISS</i>	=	international space station
<i>UTA</i>	=	University of Texas at Arlington

## I. Introduction

The ECLSS CRA currently in operation at the ISS consists of a Sabatier reactor which takes in hydrogen (H<sub>2</sub>) from the OGA and CO<sub>2</sub> from the CDRA and produces water (H<sub>2</sub>O) and methane (CH<sub>4</sub>) recovering approximately 50% of O<sub>2</sub> from metabolic CO<sub>2</sub>; the reaction that takes place on the Sabatier reactor is illustrated in Equation 1. The CH<sub>4</sub> is dehydrogenated at the PPA yielding H<sub>2</sub> and acetylene (C<sub>2</sub>H<sub>2</sub>) requiring further separation of H<sub>2</sub> from C<sub>2</sub>H<sub>2</sub>; the H<sub>2</sub>O is fed to the OGA to produce O<sub>2</sub> and H<sub>2</sub> via H<sub>2</sub>O electrolysis as illustrated in Equation 2. The H<sub>2</sub> coming from two sources, the OGA and the separation unit connected to the PPA, is recycled back to the CDRA and the O<sub>2</sub> is released into the cabin for crew consumption.



In 2016, NASA's Game Changing Development Program awarded the University of Texas Arlington (UTA) a contract to develop a Microfluidic Electrochemical Reactor (MFECR) that uses a copper-bromine electrocatalysis developed by UTA researchers<sup>1,2</sup> that reduces CO<sub>2</sub> selectively to C<sub>2</sub>H<sub>4</sub> (Equation 4) over CO and CH<sub>4</sub>, common products from similar electrochemical (EC) reduction of CO<sub>2</sub> using copper-based electrocatalysis at ambient conditions. CO and CH<sub>4</sub> are more undesired byproduct than C<sub>2</sub>H<sub>4</sub> as the formation of CO reduces O<sub>2</sub> recovery and the formation of CH<sub>4</sub> consumes more water than the formation of C<sub>2</sub>H<sub>4</sub> since it has a lower H/C ratio.



The diagram illustrates the CO<sub>2</sub> removal system for the Orion crew module. It shows the flow of air and the components involved in removing CO<sub>2</sub> and other contaminants. The process starts with Human Exhaust (CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, TC) entering the TCC System. The TCC System then feeds into the CO<sub>2</sub> Removal Assembly (CDRA). The CDRA removes H<sub>2</sub>O and CO<sub>2</sub> via adsorption on zeolite beds (swing bed adsorption). The output of the CDRA is Humidified Air (H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>), which is then fed into the Electrolytic CO<sub>2</sub> Reduction Assembly (CRA). The CRA is composed of a Microfluidic Electrochemical Reactor (MFEER) that would convert CO<sub>2</sub> to O<sub>2</sub>, ethylene and other hydrocarbons occurring at stand operating conditions and just above the freezing point of water. The CRA produces O<sub>2</sub> and Hydrocarbons. The O<sub>2</sub> is then fed back into the TCC System. The Hydrocarbons are shown as a cloud of gas. The final output is Breathable Air, which is fed back into the Human Exhaust input.

```
graph LR
    HE[Human Exhaust  
(CO2, H2O, N2,  
O2, TC)] --> TCC[TCC System]
    TCC --> CDRA[CO2 Removal  
Assembly (CDRA)]
    CDRA --> HA[Humidified Air  
(H2O, N2, O2)]
    HA --> CRA[Electrolytic CO2  
Reduction Assembly (CRA)]
    CRA --> O2[O2]
    O2 --> TCC
    CRA --> H2O[Water]
    H2O --> BA[Breathable Air]
    BA --> HE
    CDRA --> BA
    CRA --> HC[Hydrocarbons]
    HC --> Cloud(( ))
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Human Exhaust (CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, TC)

TCC System

CO<sub>2</sub> Removal Assembly (CDRA)

Humidified Air (H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>)

Electrolytic CO<sub>2</sub> Reduction Assembly (CRA)

O<sub>2</sub>

Water

Breathable Air

Hydrocarbons

CDRA removes H<sub>2</sub>O and CO<sub>2</sub> via adsorption on zeolite beds (swing bed adsorption).

Charcoal bed, catalytic oxidation, and LIOH for trace contaminant removal.

An electrolytic CRA would be composed of a Microfluidic Electrochemical Reactor (MFEER) that would convert CO<sub>2</sub> to O<sub>2</sub>, ethylene and other hydrocarbons occurring at stand operating conditions and just above the freezing point of water.

This copper-bromine electrocatalysis has a theoretical capability of recovering 73% of  $O_2$  from metabolic  $CO_2$ .  $C_2H_4$  is a more desirable byproduct than  $CH_4$  generated by the Sabatier reactor as the H/C ratio of  $C_2H_4$  is half of the H/C ratio of  $CH_4$  indicating that  $C_2H_4$  carries lower water loss than  $CH_4$  as the  $H_2$  source on both byproducts is  $H_2O$  present in the aqueous solution.

The architecture of an Electrolytic O<sub>2</sub> Recovery (EORE) system is shown in Figure 2. The EORE System would reduce the complexity by eliminating the current CRA as well as the PPA and OGA. The current CRA and other technologies that are being investigated (i.e., PPA and Bosch technologies) operate at extremely high temperatures resulting in heavy reactors and higher power consumption making the MFECR highly attractive for future exploration missions.

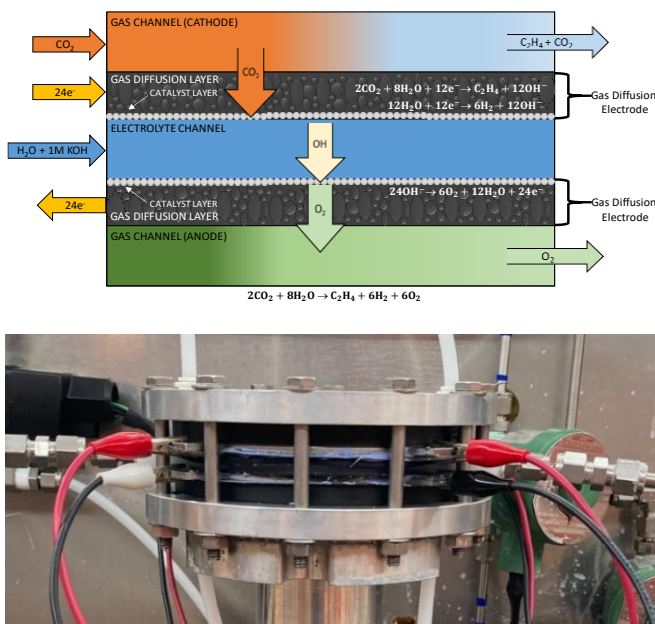
Figure 3 shows a) schematic of cross section of the MFECR cell and b) image of MFECR cell mounted in the test stand and currently being used. The MFECR cell consists of three channels. The two gas channels (anode and cathode) and the electrolyte channel are separated by a Gas Diffusion Electrode (GDE). The GDE has two embedded layers, the Gas Diffusion Layer (GDL) and the Macropore Layer (MPL) having different degree of porosity and hydrophobic coating to manage the gas and liquid phases that meet on the Catalysis Layer (CL) formed on the MPL by electrodeposited nanocomposite particles that act as electro-catalysts on the cathode (copper-bromine nanocomposite) and anode (platinum nanocomposite). The electrolyte is an alkaline solution, potassium hydroxide (KOH) and not consumed and therefore does not have to be replaced. However, H<sub>2</sub>O is consumed during the process to yield O<sub>2</sub> and the byproduct (C<sub>2</sub>H<sub>4</sub>) as illustrated in Equation 4 and needs to be added to the KOH solution to replace the consumed H<sub>2</sub>O and keep the KOH at the desired pH/concentration. In the cathode, two reactions are expected to occur, the reduction of CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> and the generation of H<sub>2</sub> from water. Both reactions form a hydroxide ion (OH<sup>-</sup>). OH<sup>-</sup> is generated at the cathode then transported by the electrical potential applied to the cell through the electrolyte to the anode where it is consumed to produce O<sub>2</sub> and H<sub>2</sub>O. During the process, O<sub>2</sub> and a mixture of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> are generated on separated cell sides (the cathode and the anode sides), which allows regeneration of H<sub>2</sub>O after feeding a fuel cell with the O<sub>2</sub> generated at the anode and H<sub>2</sub> generated at the cathode and separated from C<sub>2</sub>H<sub>4</sub>.

UTA and NASA MSFC collaborative efforts are underway to increase the O<sub>2</sub> recovery efficiency of the process to >50%, advance the technology readiness of the proposed technology to Technology Readiness Level (TRL) 4, and mature the hardware system to process 1.0 kg/day of CO<sub>2</sub>. To achieve these goals, we are currently evaluating and developing efforts on different alternatives on not only the configuration and setup of the MFECR at an Engineering Design Unit (EDU) scale but also the selection of component materials.

## II. Test Stand

The test stand, shown in Figure 4, houses an MFECR's EDU (shown in Figure 3b) and is equipped with an electrolytic cell that is fed with CO<sub>2</sub> into the cathode gas channel, N<sub>2</sub> into the anode gas channel, and an electrolyte solution into the electrolyte channel. The cathode (CO<sub>2</sub>) and anode (N<sub>2</sub>) feed streams are controlled by mass flow controllers upstream of the cell. Back Pressure Regulators (BPRs) measure the flow and controls the pressure of the anode and cathode channels outlet stream. Both anode and cathode outlet streams are fed into a condenser to remove any condensation prior to entering the BPRs and prevent any damage to the BPRs and other components downstream.

The electrical power utilized by the EDU's electrolytic cell is provided by a DC power supplier directly attached to the anode and cathode contacts of the cell. A gas chromatograph (GC) samples the inlet/outlet anode or cathode streams to measure the amount of C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> produced in the cathode channel and O<sub>2</sub> produced in the anode channel to determine the chemical conversion achieved by the electrolytic cell. Besides C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> components, the GC has been calibrated to detect and measure also undesired (but of not necessarily unexpected) components, such as CO and CH<sub>4</sub>. The GC also has been calibrated to detect and measure C<sub>2</sub>H<sub>2</sub>, an unexpected but not undesirable component (H/C ratio of unexpected C<sub>2</sub>H<sub>2</sub> is lower than H/C ratio of expected C<sub>2</sub>H<sub>4</sub> component).



**Figure 3. a) Schematic of cross section of the MFECR cell, b) Image of MFECR's EDU mounted in the test stand.**

The electrolyte solution is supplied to the EDU's EC cell using a peristaltic pump. The peristaltic pump extracts the electrolyte solution from a tank to feed the electrolyte channel returning the EDU's outlet solution stream to the tank. To be able to run the electrolyte solution at temperatures below ambient, the electrolyte passes through a chiller immediately downstream of the electrolyte pump; a cold electrolyte favors the CO<sub>2</sub> solubility increasing the CO<sub>2</sub> availability on the EC site. The electrolyte flow rate is measured downstream of the cell using an ultrasonic sensor. Inline pH meters are used to measure the concentration of the electrolyte before and after passing through the EDU. An additional peristaltic pump is used to supply H<sub>2</sub>O to the electrolyte based on a calculated value of H<sub>2</sub>O consumed in the process to ensure the desired electrolyte pH/concentration.

Solenoid valves are located throughout the test stand to automate the process. Thermocouples are attached to the cell to monitor the temperature throughout the cell and the heat generated during the process. A H<sub>2</sub> sensor is installed at the top of the hood to warn if 0.5% concentration of H<sub>2</sub> has been reached and to initiate shutdown of the system if 1% concentration has been reached. Control of the entire MFECR process including safety monitoring and test data logging is accomplished by using LabVIEW software.



**Figure 4. Test stand at MSFC housing a MFECR at EDU scale.**

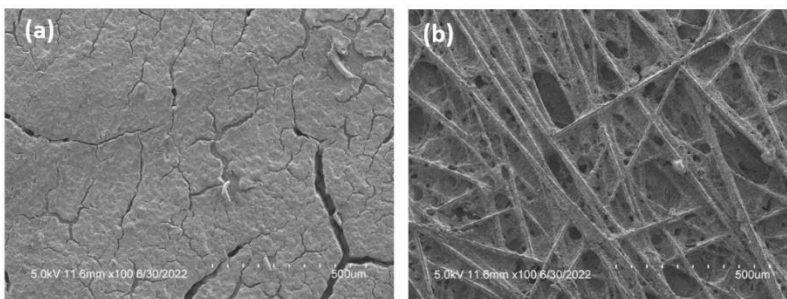
### III. EDU Electrochemical Cell

#### A. Gas-feed CO<sub>2</sub> Electrolyzer

The current challenge of CO<sub>2</sub>R is designing an electrolyzer that can operate at high Faradaic efficiency, high current density, and low cell voltage. The CO<sub>2</sub>R reactor must be also scalable and operate steadily for tens of thousands of hours. Widely used liquid-fed electrolyzer bear CO<sub>2</sub> mass-transfer limitations that lead to an increase in the undesired hydrogen evolution reaction (HER) at high current densities. The GDE overcomes this limitation as it allows CO<sub>2</sub> to permeate the GDL and the MPL to reach CL formed with deposited electrocatalysis.

GDEs have been mostly used in two major types of gas-fed CO<sub>2</sub> electrolyzer. In the first electrolyzer type, the cathode GDE is in direct contact with an ionomer membrane and exchanges ions with the anode and a flowing electrolyte<sup>4</sup>. Ionomer membranes are also named as membrane electrode assembly (MEA). In the second electrolyzer type, both GDEs are in direct contact with the electrolyte allowing better control of the ionic environment at the reaction interface<sup>5</sup>.

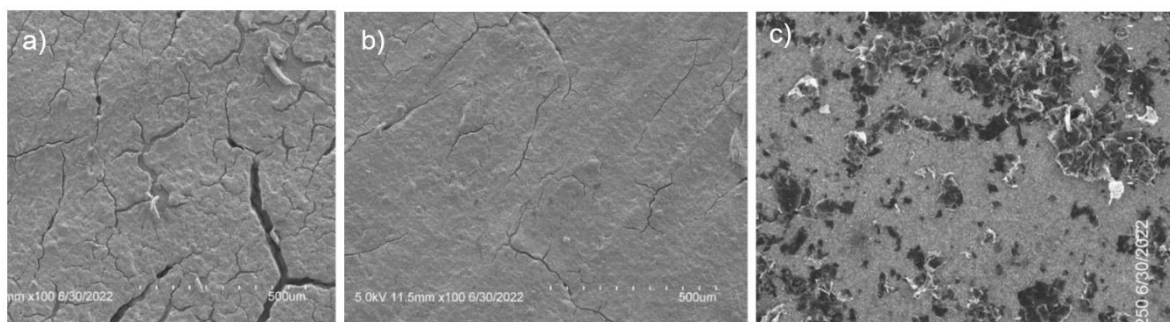
We are currently using Sigracet 28BC GDE, a commercially available non-woven carbon paper with a GDL composited with a MPL that has been treated with poly-tetra-fluoro-ethylene (PTFE) to 5 wt%. It has a total thickness of 235 μm (microns). The hydrophobic treatment produces water repellent properties which prevent the highly porous GDE backings from flooding and actively support the water management of the electrolyzer. Figure 5 shows SEM images of both surfaces of the Sigracet 28BC GDE that correspond to the outer surfaces of the MPL (a) and the GDE (b). The hydrophobic nature of the MPL allows the aqueous electrolyte not only to avoid flooding the GDE but also to adjust the amount of electrolyte within the gas-electrocatalysis interface formed in the CL and where heterogeneous EC reactions takes place. Unfortunately, the MPL hydrophobic nature is not enough to prevent the gas



**Figure 5. SEM images of both surfaces of the Sigracet 28BC GDE that correspond to the outer surfaces of the MPL (a) and GDE (b).**



leaking through the MPL's cracks into the electrolyte; Figure 5a clearly shows the cracks on the MPL of a Sigracet 28BC GDE. We are currently testing and evaluating both types of gas-fed CO<sub>2</sub> electrolyzer mentioned above. In the first type (GDE is in direct contact with an ionomer membrane) the ionomer membrane also serves as a physical barrier to restrain the gas from leaking through the MPL's cracks and causing gas leak/seepage into the electrolyte. To test the second type (GDE is in direct contact with the electrolyte) the MPL's cracks need to be filled and sealed to mitigate the gas leak into the electrolyte; this should minimize the electrolyte seepage into the cathode GDL and prevent flooding the CL to yield stable electrochemical operation for the cell. The GDE suppliers have recognized there is no commercial GDL targeted for EC CO<sub>2</sub>R and offer modified GDE as an option.



**Figure 6. SEM images of Sigracet 28BC MPL surface: a) unmodified, (b) treated with Vulcan carbon black, and c) treated with graphene.**

This is a developmental product with improvements based on comments received by researchers worldwide after testing the first generation offering. This GDE is comprised of a hybrid MPL, where the surface cracks of the original Sigracet 28BC are post-filled with a mixture of Vulcan carbon black or graphene nanoparticles and Teflon Fluorinated Ethylene Propylene Dispersion 121 (FEPD 121) as the binding agent. Figure 6 shows SEM images of the MPL surface of the Sigracet 28BC GDE after being treated with Vulcan carbon (b) and graphene (c). It is clear from Figure 6 that the original MPL's cracks (Figure 6a) are mostly filled with the mixture of Vulcan carbon black (Figure 6b) or graphene (Figure 6c) and FEPD 121 as the binding agent.

Experimental tests with gas-fed CO<sub>2</sub> electrolyzer having the MPL in direct contact with the electrolyte and GDEs treated with Vulcan carbon black or graphene did not show leak of gas through the MPL to the electrolyte, because not only the MPL's cracks were significantly reduced but also because the operating gas pressure on the MFECR was also reduced below atmospheric pressure.

The two types of gas-fed CO<sub>2</sub> electrolyzer stated above are currently being tested. For Type 1 electrolyzer in which the MPL/CL is in direct contact with the ionomer membrane, three different ionomer membranes having similar thicknesses (around 70  $\mu$ m) are being evaluated; the three ionomer membranes are Fumasep, Sustainion, and Bettergy.

Suspension versions of these three membranes are also commercially available and were preliminarily tested but gas leak into the electrolyte was observed with all three suspensions applied and cured directly to the unmodified Sigracet 28BC. For type II electrolyzer in which the MPL/CL is in direct contact with the electrolyte, the two modified Sigracet 28 BC GDEs with Vulcan carbon black and graphene are currently being tested. The suspension version of the three ionomer membranes stated above will be applied to the MPL/CL and test them in this type II electrolyzer to evaluate the suspension effect on reducing the MPL cracks and the ionic conductivity in the MPL/CL gas-electrocatalysis interface. The ionomer suspension is applied throughout the MPL/CL surface and then put it in an oven at 90-120 Celsius for 20-45 minutes to evaporate the solvent and allow the adhesion of the ionomer polymer on the MPL/CL surface.

Gas-fed CO <sub>2</sub> electrolyzer		Run	Sigracet 28BC		Ionomer Membrane	Ionomer Suspension
I	MPL direct contact with ionomer	1	Unmodified		Fumasep	No
		2			Bettergy	No
		3			Sustainion	No
II	MPL direct contact with electrolyte	4	Modified	FEPD 121 & carbon black	No	No
		5				Yes
		6		FEPD 121 & graphene	No	No
		7				Yes

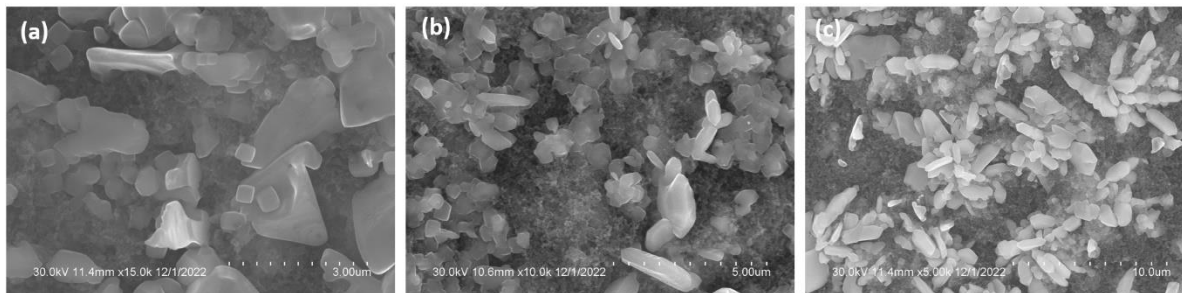
**Table 1. Test data matrix to evaluate two types of gas-fed CO<sub>2</sub> electrolyzer.**

Table 1 summarizes the test data matrix we are using to evaluate both gas-fed CO<sub>2</sub> electrolyzer types. The criteria to select the best electrolyzer setup includes CO<sub>2</sub> reduction efficiency, highest Faradaic efficiency, and highest current density.

## B. Cathode electrocatalysis

Several electrocatalysis derived from main group and transition metals have been deployed for CO<sub>2</sub> reduction. Of these, copper is unique in its ability to reduce CO<sub>2</sub> to hydrocarbons at ambient temperature and pressure. However, one of the main challenges with copper is that it lacks selectivity for a given hydrocarbon product yielding a mixture of hydrocarbons and it is prone to reduce electrocatalytic activity for CO<sub>2</sub> reduction decreasing rapidly after some tens of minutes of electrolysis<sup>3</sup>.

Other metal-based electrocatalysis alternatives for CO<sub>2</sub> reduction are prone to yield CO, undesirable for O<sub>2</sub> recovery from metabolic CO<sub>2</sub>, besides useful hydrocarbons, as well as issues with rapid decrease in CO<sub>2</sub> reduction within tens of minutes during electrolysis. UTA researchers developed a unique electrocatalysis composed of copper oxide (Cu<sub>2</sub>O) – copper bromide (CuBr) to be electrodeposited on the MPL of a GDE to form a CL and convert CO<sub>2</sub> to selectively C<sub>2</sub>H<sub>4</sub> over other hydrocarbons and CO.

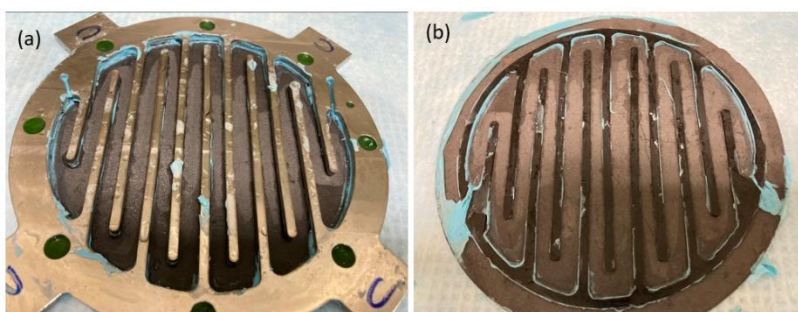


**Figure 7. SEM images obtained during the growth of hybrid Cu<sub>2</sub>O-CuBr up to selected electrodeposition charges: (a) after 10 min, EDQ 2.0 C/cm<sup>2</sup>, (b) 20 min, EDQ 4.0 C/cm<sup>2</sup>, (c) 30 min, EDQ 6.0 C/cm<sup>2</sup>.**

SEM images obtained during the growth of Cu<sub>2</sub>O-CuBr electrocatalysis in time up to the selected electrodeposition charge (6.0 C/cm<sup>2</sup>) are shown in Figure 7 illustrating the morphology and texture of deposition after 10 (a), 20 (b) and 30 (c) minutes of electrodeposition at EDQ values of 2, 4, and 6 C/cm<sup>2</sup> respectively.

## C. Anode electrocatalysis

Platinum (Pt) was electrochemically deposited on regular Sigracet 28BC GDE and used it as anode in the gas-fed CO<sub>2</sub> electrolyzer. O<sub>2</sub> generated at the anode led to carbonization of the GDE underneath the wall of the serpentine wall as shown in Figure 8 and corroborated by the GC detecting CO by the GC.



**Figure 8. Carbonization on anode GDE underneath the serpentine wall of the Ni-fabricated current distributor used also as gas channel.**

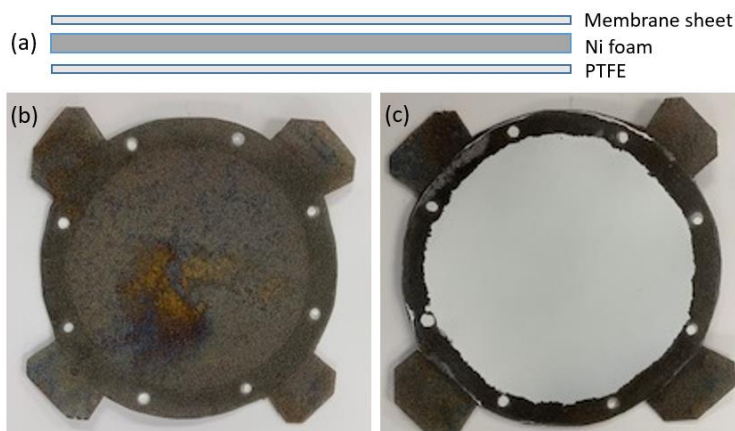
Figure 8 shows the carbonization on anode GDE underneath the serpentine wall of the Ni-fabricated electrical-current distributor used as gas channel in the anode (and the cathode). Figure 8a shows the current distributor as it is assembled in the gas-fed CO<sub>2</sub> electrolyzer. The GDL side of Sigracet 28BC GDE is underneath the current distributor (and the MPL/CL side of the GDE in contact with the electrolyte); Figure 8b shows the GDE surface after removing the electrical-current distributor. It is clear from Figure 8b that GDE carbonization happened underneath the serpentine wall of the current distributor as black path is formed along and underneath the serpentine wall. To determine if electrical current biased on the GDL region underneath the serpentine wall or/and Ni acting as catalysis was causing the carbonization, tests were conducted having a gasket and silicone application underneath the serpentine.

Carbonization underneath the serpentine wall still happened indicating that the biased carbonization might be due to the compression of the wall against the GDE leading to alteration of the configuration including porosity, void fraction, and actual density and the retention of the O<sub>2</sub> generated at CL.

#### D. Alternative anode development

To achieve high Oxygen Evolution Reaction (OER) current densities and overcome slow kinetics of the OER in the anode requires metal electrodes that exhibit high electrocatalytic activity and require low overpotential. In this regard, we use morphological engineering of three-dimensional (3D) nickel foam and electrochemically anodize it as a strategy for increasing the number of active surface area and enhance the corrosion resistance. Electrochemical anodization is very simple and attractive technique to form nanopores oxide layer using various metal substrates including, Al, Ti, and others.

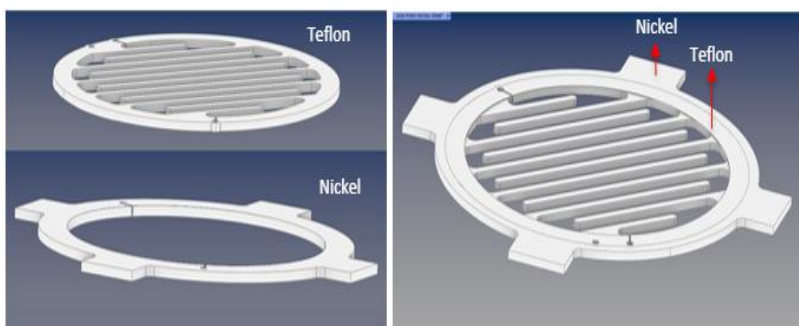
Electrochemical anodization experiments were performed using as-purchased nickel foil (purity > 99.9 wt%, thickness 1.6 mm, surface density 346 g/m<sup>2</sup>, MTI Corporation) was cleaned by soak in concentrate HCl acid and sonicated in DI water, ethanol for 20 minutes each and dried under flowing N<sub>2</sub> gas. The cleaned Ni foil was anodized in a two-electrode electrochemical cell at 30 to 60 V using Sorensen Ametek power supply (model XG 30-50) and the anodic current was recorded. During anodization in an electrolyte solution containing hydroxide, ethylene glycol, and water. Stainless steel foil was used as the counter electrode. The anodized Ni foam samples were rinsed in DI water to remove the residual electrolyte and dried under N<sub>2</sub> gas, following by thermal annealing in a muffle furnace. This process results in annealed NiO anode. Then a thin membrane layer and PTFE film were placed on top and bottom of the annealed NiO anodes, respectively. The silicone glue was put on the edge of anode to glue the membrane layer and PTFE film with the anode and allowed to cure overnight at room temperature. The cross-section diagram of the composite anode is shown in Figure 9a, the annealed NiO foam anode and the PTFE film covering the annealed NiO foam are shown in Figures 9b and 9c respectively.



**Figure 9. (a) The composite anode cross-section diagram, (b) The annealed NiO foam anode and, (c) The composited NiO foam anode.**

#### E. Alternative gas-fed CO<sub>2</sub> electrolyzer with composite electrical current distributor

Apparent mild carbonization also happened using the alternative Ni-foam composite anode described above, not underneath the current-collector serpentine walls as it happened with the platinized GDE anode, but on the wall's edges in contact with the anode's membrane sheet leading to the suspect of undesired Ni-triggered catalytic activity.



**Figure 10. Alternative Teflon-Nickel composite electrical-current distributor for gas-fed CO<sub>2</sub> electrolyzer.**

We have redesigned the Ni-fabricated current distributor of the EDU to mitigate carbonization underneath the collector's serpentine walls on both anode types tested, platinized GDE and nickel-foam composite. The new design



will have Teflon serpentine wall with a clearance underneath the wall to be filled with cured silicone to mitigate the compression on the GDE.

### References

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